

Chaotic Scattering Theory of Transport and Reaction-Rate Coefficients

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ABSTRACT

The chaotic scattering theory is here extended to obtain escape-rate expressions for the transport coefficients appropriate for a simple classical fluid, or for a chemically reacting system. This theory allows various transport coefficients such as the coefficients of viscosity, thermal conductivity, etc., to be expressed in terms of the positive Lyapunov exponents and Kolmogorov-Sinai entropy of a set of phase space trajectories that take place on an appropriate fractal repeller. This work generalizes the previous results of Gaspard and Nicolis for the coefficient of diffusion of a particle moving in a fixed array of scatterers.

1 Introduction

One of the remarkable results of recent studies of non-equilibrium processes taking place in large systems has been the establishment of new connections between non-equilibrium statistical mechanics, and dynamical system theory [1, 2]. Although much more work needs to be done before these connections are clear and well established, some of the new results establish a direct connection between quantities of interest for the statistical mechanics of irreversible processes, such as transport coefficients, and quantities of interest for the dynamical description of the same system, such as Lyapunov exponents, and Kolmogorov-Sinai entropies. Here we will restrict our discussion to classical systems for which a reasonable level of understanding has been achieved.

One method for developing such connections, which has been developed by Hoover, Posch and coworkers [3], and by Evans, Cohen, Morris and coworkers [4], is based on a study of systems that are maintained in non-equilibrium steady states by means of specially constructed external or internal “forces” and a thermostat that removes energy generated in the system by the special forces. This method leads to interesting connections between transport coefficients, such as the coefficients of diffusion or viscosity, and the Lyapunov exponents of the thermostatted, forced system. For the case of a thermostatted single particle moving (in two dimensions) in a periodic Lorentz gas under the action of an electric field, the connection between the diffusion coefficient, or the electrical conductivity, and the (two) Lyapunov exponents was studied by Baranyi, Evans, and Cohen [5], and rigorous results establishing this connection were obtained by Chernov, Eyink, Lebowitz and Sinai [6]. One feature of this approach is that a Hamiltonian description of the system is not possible, due to the introduction of the thermostat and the question naturally arises as to whether a connection

of the sort described is possible for purely Hamiltonian systems.

This question was answered in the affirmative, for the case of a classical particle moving in an environment of fixed scatterers, by Gaspard, Nicolis, and coworkers [7, 8]. They were able to show that the diffusion coefficient of the moving particle could be obtained in terms of the escape rate for the particle from a bounded region of the scatterers. This escape rate, in turn, is obtained – following arguments of Kantz and Grassberger [9], Bohr and Rand [10], Tel and coworkers [11], Grebogi, Ott, and Yorke [12] – in terms of the positive Lyapunov exponents and KS-entropy that characterize the set of orbits of the moving particle that are trapped forever in the bounded region occupied by the scatterers. This set of “trapped” orbits form a fractal set of trajectories of the moving particle, and is referred to as the “repeller” [13]. The relation between the diffusion coefficient, D , for the moving particle and the dynamical quantities on the repeller is given by [7]

$$D = \lim_{L \rightarrow \infty} \left(\frac{L}{\pi} \right)^2 \left[\sum_{\lambda_i > 0} \lambda_i(L) - h_{\text{KS}}(L) \right]. \quad (1.1)$$

Here, we suppose that the scatterers are confined to a slab of width L in one dimension, and of infinite length in perpendicular spatial directions; $\sum_{\lambda_i > 0} \lambda_i(L)$ is the sum over all *positive* Lyapunov exponents for trajectories on the repeller, and $h_{\text{KS}}(L)$ is the KS-entropy for trajectories on the repeller. We assume, usually without proof, that the system has ergodic properties such that the λ_i do not depend on the particle trajectory on the repeller. We also note that for the open systems considered here (i. e. particles not on the repeller escape from the region containing the scatterers), the KS-entropy on the repeller does *not* equal the sum of the positive Lyapunov exponents, and the difference is of order L^{-2} for large L , if the diffusion coefficient exists. The escape-rate expression for the diffusion coefficient has been

evaluated explicitly for a two-dimensional periodic Lorentz gas [8], for a two-dimensional multibaker transformation [14], and for a variety of one-dimensional maps [15].

In the preceding discussion, the diffusion process is actually considered as a chaotic scattering occurring in a large but finite system. Several recent works have been devoted to chaotic scattering and have elucidated the role of the fractal repeller in this phenomenon [16]. Usually, chaotic scattering is envisaged on a small scatterer containing a few scattering centers [11, 16, 17]. However, it was shown that chaotic scattering becomes controlled by diffusion when the scatterer becomes large enough. Remarkable relations then exist between the properties of scattering and those of diffusion, which have recently been described in some detail [18].

It is the purpose of this paper to extend the chaotic scattering theory and, in particular, the escape-rate formalism to include other transport coefficients, and to include a treatment of chemical reaction-rate coefficients. This is accomplished by showing that the basic ideas used to derive the expression for the diffusion coefficient of a moving particle can be easily extended to apply to other transport and reaction-rate coefficients as well.

In the next Secs. 2 and 3, we present the derivation of the escape-rate expressions for transport and reaction rate coefficients. This derivation is based on the fact that all of these coefficients can be related to the average mean square displacement of some appropriate dynamical quantity. In Sec. 4 of the paper, we outline some outstanding and interesting problems related to this work. A careful discussion of the theory for chemical reaction rates is given in Appendix A. Derivations of the relation between the escape rate of a dynamical quantity from a bounded region and the Lyapunov exponents and KS-entropy has been given in the literature for systems of a small number of dimensions [1, 9, 10, 11, 12]. In a separate

paper [19], we will review this derivation, so as to extend it to systems with many degrees of freedom, to systems that may be of nonhyperbolic type, and to illustrate the method with applications to lattice gas automata and to hard sphere gas systems.

2 Transport Coefficients and their Helfand Moments

We begin by constructing a large system of N particles governed by Hamilton's equation of classical mechanics

$$\dot{\mathbf{q}} = \frac{\partial H}{\partial \mathbf{p}}, \quad \dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{q}}, \quad (2.1)$$

where (\mathbf{q}, \mathbf{p}) are the positions and momenta of the particles. We assume that these particles are contained in a rectangular domain of volume V . At the borders, we may consider either hard walls of infinite mass or periodic boundary conditions. In the latter case, the total momentum is conserved in addition to the total energy. Moreover, to simplify the relation with ergodic theory, we use the microcanonical ensemble and work on energy shells $H = E$.

In the large system limit ($N, V \rightarrow \infty$ with $N/V = n$), irreversible processes in such a classical many-body system may be described by hydrodynamic equations such as the Navier-Stokes equations, or the diffusion equation, the chemical kinetic equations ruling the time evolution of chemical concentrations, or the equations of electrical conductivity which incorporate Ohm's law. These phenomenological equations contain dissipative terms which are dependent on transport and rate coefficients. The aim of nonequilibrium statistical mechanics is to obtain these coefficients in terms of the microscopic Hamiltonian equations. Since the work of Maxwell and Boltzmann, several methods have been developed to calculate these coefficients. The most general method, developed by Green and Kubo [20, 21], is the

time correlation function approach whereby the transport and rate coefficients, are given as time-integrals of autocorrelations of the fluxes,

$$\alpha = \int_0^\infty \lim_{V \rightarrow \infty} \langle J_0^{(\alpha)} J_t^{(\alpha)} \rangle dt , \quad (2.2)$$

where $J_t^{(\alpha)}$ is the flux at time t corresponding to the coefficient α . It is a function of the canonical variables (\mathbf{q}, \mathbf{p}) and is obtained by solving the equations of motion for a time t after an initial time so that

$$J_t^{(\alpha)}(\mathbf{q}, \mathbf{p}) = J_0^{(\alpha)}[\Phi^t(\mathbf{q}, \mathbf{p})] , \quad (2.3)$$

where Φ^t denotes the flow in phase space induced by Hamiltonian equations (2.1). We can express this in terms of an N -particle streaming operator

$$J_t^{(\alpha)} = \exp(-t\hat{L}) J_0^{(\alpha)} , \quad (2.4)$$

with the Liouvillian operator given in terms of a Poisson bracket expression $\hat{L} = \{H, \cdot\}$. The average $\langle \cdot \rangle$ in equation (2.3) is taken over a microcanonical ensemble in our case.

It will be useful for us to apply the formulation of the Green-Kubo expressions, as obtained by moments $G_t^{(\alpha)}$ such that the fluxes $J_t^{(\alpha)}$ are derivatives, as [22]

$$J_t^{(\alpha)} = \frac{d}{dt} G_t^{(\alpha)} , \quad (2.5)$$

An integration by parts shows that

$$\langle (G_t - G_0)^2 \rangle = \int_0^t \int_0^t \langle J_{t'} J_{t''} \rangle dt' dt'' = 2t \int_0^t \left(1 - \frac{\tau}{t}\right) \langle J_0 J_\tau \rangle d\tau . \quad (2.6)$$

Accordingly, if the following condition is satisfied

$$\lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \tau \langle J_0 J_\tau \rangle d\tau = 0 , \quad (2.7)$$

we obtain the equality

$$\lim_{t \rightarrow \infty} \frac{\langle (G_t - G_0)^2 \rangle}{2t} = \int_0^\infty \langle J_0 J_\tau \rangle d\tau . \quad (2.8)$$

As a consequence, the transport and rate coefficients are also given by [22]

$$\alpha = \lim_{t \rightarrow \infty} \frac{1}{2t} \lim_{V \rightarrow \infty} \langle [G_t^{(\alpha)} - G_0^{(\alpha)}]^2 \rangle . \quad (2.9)$$

Table I. Helfand's moments.

<i>process</i>	<i>moment</i>
self-diffusion	$G^{(D)} = x_i$
shear viscosity	$G^{(\eta)} = \frac{1}{\sqrt{V k_B T}} \sum_{i=1}^N x_i p_{iy}$
bulk viscosity ($\psi = \zeta + \frac{4}{3}\eta$)	$G^{(\psi)} = \frac{1}{\sqrt{V k_B T}} \sum_{i=1}^N x_i p_{ix}$
heat conductivity	$G^{(\kappa)} = \frac{1}{\sqrt{V k_B T^2}} \sum_{i=1}^N x_i (E_i - \langle E_i \rangle)$
charge conductivity	$G^{(e)} = \frac{1}{\sqrt{V k_B T}} \sum_{i=1}^N e Z_i x_i$
chemical reaction rate	$G^{(r)} = \frac{1}{\sqrt{V k_B T}} (N^{(r)} - \langle N^{(r)} \rangle)$

In Table I we list moments appropriate for each transport or rate coefficient, where $E_i = \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j(\neq i)} V_{ij}$ is the energy of particle i and V_{ij} is the potential energy of interaction between particles i and j . Appendix A describes in more detail the case of chemical reactions.

Eq. (2.9) shows that, in the case the transport or rate coefficients are well defined (i.e. are positive and finite), Helfand's moments undergo a diffusive type of motion along the axis of the moment $G^{(\alpha)}$. Therefore, the moment may be considered as a random variable having a probability density $p(g)$ obeying a diffusion-type equation, in an equilibrium ensemble

$$\frac{\partial p}{\partial t} = \alpha \frac{\partial^2 p}{\partial g^2} , \quad (2.10)$$

with the transport or rate coefficient α a diffusion coefficient. This equation is the Fokker-Planck equation governing the equilibrium fluctuations of the Helfand moments. Equivalently, one can recover Eq. (2.9) by supposing that the moments satisfy a Langevin stochastic differential equation

$$\dot{G}^{(\alpha)} = J_t^{(\alpha)} , \quad (2.11)$$

where the flux $J_t^{(\alpha)}$ is a white noise

$$\langle J_t^{(\alpha)} \rangle = 0 , \quad \langle J_0^{(\alpha)} J_t^{(\alpha)} \rangle = 2\alpha \delta(t) . \quad (2.12)$$

It is important to note that equations (2.10) or (2.12) are to be considered as a simple representation of the results of the time correlation function method for time scales which are much longer than the time necessary for the time correlation functions of the microscopic currents to decay to zero. We suppose that this approach applies to situations where, for example, long time tails in the correlation functions decay sufficiently rapidly for the transport coefficients as defined by Eq. (2.2) to exist. In this way we can still treat processes which are diffusive on long time scales, but have correlations on shorter time scales. Accordingly,

the existence of a flux autocorrelation function which differs from a delta distribution on short time scales is still perfectly compatible with the validity of the diffusion-type equation, (2.10), on long time scales.

In this discussion we have tacitly assumed that we consider a physical system in the proper thermodynamic limit. However, for systems of finite volume, there is an upper limit on the times we can consider because the ranges of variation of the Helfand moments are bounded. For example, if the system consists of hard spheres placed in a cubical box of length L on a side, the positions of each particle vary only in the interval

$$-\frac{L}{2} \leq x_i, y_i, z_i \leq +\frac{L}{2}, \quad (2.13)$$

while the momenta can only take values in the interval

$$-\sqrt{2mE} \leq p_{ix}, p_{iy}, p_{iz} \leq +\sqrt{2mE}, \quad (2.14)$$

where $E = E_{\text{tot}} = \frac{3}{2}Nk_B T$ is the total energy. Similarly, the energy of a particle can only lie in the range

$$0 \leq E_i \leq \frac{3}{2} k_B T N. \quad (2.15)$$

Because of these bounds, the moments are always of bounded variation in the interval

$$|G^{(\alpha)}| \leq C N^{\delta^{(\alpha)}}, \quad (2.16)$$

where C is some constant, and $\delta^{(\alpha)}$ are positive exponents which are respectively $\delta^{(\text{D})} = 1/3$, $\delta^{(\eta)} = 4/3$, $\delta^{(\psi)} = 4/3$, $\delta^{(\kappa)} = 11/6$, $\delta^{(\text{e})} = 5/6$, and $\delta^{(\text{r})} = 1/2$, for three-dimensional

gases. Accordingly, the range of variation of the moments grow with the size of the system, when the density and other intensive variables are kept constant. Of course, most variations of the Helfand moments will be due to microscopic motions of the particles and thus will be much smaller than the bounds in Eq. (2.16). At any rate, as the system gets larger, we expect that the diffusive-like behavior of the moments, described by Eq. (2.10), will be valid over increasingly larger regions of variations of the $G^{(\alpha)}$.

After the discussion about the limited range over which the Helfand moments obey the diffusive-type equation (2.10) for finite systems, we may proceed.

3 Escape-Rate Formalism

Within the range of validity of (2.10), we may set up a problem of first passage for the moment $G^{(\alpha)}$ corresponding to the transport or rate processes of coefficient α . We consider a statistical ensemble formed by copies of the system which we assume to be at equilibrium and microcanonical at total energy E (and eventually at fixed total momentum in the case of periodic boundary conditions: $\mathbf{P}_{\text{tot}} = \sum_{i=1}^N \mathbf{p}_i$). For each copy, the motion of the Hamiltonian system (2) is integrated from the initial conditions and the Helfand moment is calculated along the trajectory. At each time, we count the number of copies, $\mathcal{N}^{(\alpha)}(t)$, for which the moment is still in the following interval

$$-\frac{\chi}{2} \leq G_t^{(\alpha)} \leq +\frac{\chi}{2}, \quad (3.1)$$

where the size of the interval χ is sufficiently large to be in the regime of diffusion of the moment but not too large with respect to the total variation interval of the moment allowed by the finiteness of the system. We are here defining a problem of first passage which can be

solved using the eigenvalues and eigenfunctions of the Fokker-Planck equation (2.10) with the boundary conditions

$$p(-\chi/2) = p(+\chi/2) = 0 . \quad (3.2)$$

The solution of this eigenvalue problem is well known to be

$$p(g, t) = \sum_{n=1}^{\infty} c_n \exp(-\gamma_n^{(\alpha)} t) \sin\left(\frac{\pi n}{\chi} g\right) , \quad \text{with} \quad \gamma_n^{(\alpha)} = \alpha \left(\frac{\pi n}{\chi}\right)^2 , \quad (3.3)$$

where the constants c_n are fixed from the initial probability density $p(g, 0)$. The number of copies of the statistical ensemble which are still in the interval (3.1) is then given by

$$\mathcal{N}^{(\alpha)}(t) = \int_{-\chi/2}^{+\chi/2} p(g, t) dg . \quad (3.4)$$

At long times, the decay is dominated by the slowest decay mode corresponding to the smallest decay rate $\gamma_1^{(\alpha)}$ which defines the escape rate of the moment out of the interval (3.1),

$$\gamma_1^{(\alpha)} = \alpha \left(\frac{\pi}{\chi}\right)^2 . \quad (3.5)$$

We are now in position to establish a relationship with the deterministic dynamics. The Hamiltonian classical motion of the many-body system is chaotic in many cases. This property has been proved by Sinai and coworkers for some simple hard sphere gas models [23, 24]. Also strong numerical evidence exists which shows that half of the Lyapunov exponents are typically positive in systems of statistical mechanics like the Lennard-Jones gas at room temperatures [25]. We suppose that the decomposition of phase space into ergodic

components is understood and that, beside the decomposition on the known constants of motion, there is only a single main ergodic component.

We consider the set of all the trajectories for which the Helfand moment remains forever within the interval (3.1). Because most of the trajectories are expected to exit this interval, the trapped trajectories must be exceptional and highly unstable forming a set of measure zero with respect to the microcanonical probability measure. Based on earlier work on diffusion in the Lorentz gas and in related models and on the basis that the trajectories are typically of saddle type in systems of statistical mechanics [7, 8, 14, 17, 18], we assume that the set of trajectories is a fractal repeller. Indeed, this set is of vanishing measure but may still contain an uncountable infinity of periodic and nonperiodic trajectories. A set satisfying these conditions is necessarily a fractal [1]. Moreover, it is composed of unstable trajectories of saddle type so that it forms a repeller (of saddle type) in phase space. These properties can be proved for particular models like the multibaker area-preserving map [14] as well as the array of disk scatterers composing the periodic Lorentz gas. Accordingly, it seems reasonable to assume that, for more general systems, such as a gas of hard spheres the set of trajectories for which the moments satisfy Eq. (3.1), form a fractal repeller, with properties to be described in the next paragraph.

A fractal repeller is characterized by different quantities and, especially, by an escape rate which is the deterministic analogue of the escape rate obtained in the preceding first-passage problem. Moreover, in chaotic systems, the escape rate is related to the sum of positive Lyapunov exponents minus the Kolmogorov-Sinai entropy per unit time if these quantities are well defined and positive [1, 9, 10, 11, 17]. These quantities are evaluated for the natural invariant probability measure whose support is the fractal repeller. For the natural invariant

measure, each cell of phase space has a weight which is inversely proportional to the local Lyapunov numbers (stretching factors). Therefore we have [1, 9, 10, 11, 12, 14, 17]

$$\gamma_1^{(\alpha)} = \sum_{\lambda_i > 0} \lambda_i(\mathcal{F}_\chi^{(\alpha)}) - h_{\text{KS}}(\mathcal{F}_\chi^{(\alpha)}) , \quad (3.6)$$

where we denote by $\mathcal{F}_\chi^{(\alpha)}$ the fractal repeller formed by the trapped trajectories for which the Helfand moment $G_t^{(\alpha)}$ remains forever in the interval (3.1).

Combining the deterministic result (3.6) with the statistical result (3.5), we obtain the relationship

$$\alpha = \lim_{\chi \rightarrow \infty} \left(\frac{\chi}{\pi} \right)^2 \lim_{V \rightarrow \infty} \left[\sum_{\lambda_i > 0} \lambda_i(\mathcal{F}_\chi^{(\alpha)}) - h_{\text{KS}}(\mathcal{F}_\chi^{(\alpha)}) \right] , \quad (3.7)$$

where the limit $V \rightarrow \infty$ denotes the thermodynamic limit to be taken before the limit $\chi \rightarrow \infty$ which is internal to the system.

With Table I, Eq. (3.7) shows how a general transport or rate coefficient can in principle be related to the Lyapunov exponents and the Kolmogorov-Sinai entropy of a fractal repeller. This fractal repeller is the phase space object corresponding to the escape process of the Helfand moment associated to the transport or rate coefficient. In this way, a connection is established between statistical and mechanical considerations in phase space.

A remark is now in order about the magnitude of the quantities appearing in (3.7). The sum of positive Lyapunov exponents and the KS-entropy per unit time are very large, of the order of the number of particles times the inverse of a typical kinetic time scale [26]. On the other hand, the escape rate, which is the difference between two such large numbers, has a much smaller magnitude given by the time scales characteristic of hydrodynamics. In this way, the kinetic and hydrodynamic levels are naturally connected with a formula like (3.7).

4 Conclusion

We have shown that all of the transport coefficients for a simple fluid and that chemical reaction rate coefficients can be expressed in terms of an escape rate from an appropriate fractal repeller. This completes a line of argument initiated by previous work on the coefficient of diffusion for a particle moving in a periodic Lorentz system [7], and for a multibaker map [14]. In a separate paper [19], we will show how the escape-rate formula can be applied to several classes of dynamical systems like the hard sphere gas and the lattice gas automata. We also describe there a large deviation formalism which allows us to extend the application of the escape rate formula (3.7) from hyperbolic to nonhyperbolic systems, in particular, using the Ruelle pressure function. It now remains to apply this formalism to a number of examples in order to understand the physical and mathematical consequences of this approach to transport in fluid systems. Applications of this formalism to certain types of one-dimensional diffusion problems will be presented in [15], and applications to Lorentz lattice gas cellular automata will be presented in [27]. Many further applications are possible.

Many interesting problems remain open in the present context, in particular:

- a) To provide experimental evidence for the microscopic chaos at the basis of the present theory. Suggestions along this line has been discussed elsewhere [28].
- b) To provide a more rigorous mathematical derivation of the escape-rate formalism used here.
- c) To establish the connection between this formalism and those based upon period-orbit theory [29] and upon a study of eigendistributions of the Liouville operator, and Ruelle

resonances [14, 30, 31]. Already, such a connection has been discussed elsewhere [18] where it was shown for the multibaker model that the diffusive-like eigendistributions of the Liouville operator shares self-similar properties with the fractal repeller underlying diffusion. Moreover, both approaches make use of the leading eigenvalues (3.5) of the Liouville operator and of its dependence on the wavenumber of the diffusive eigenmode ($k = \pi/L$).

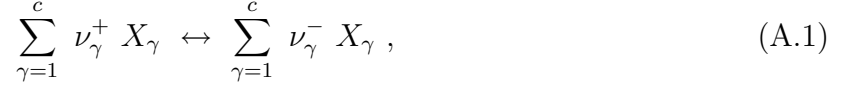
- d) To extend this formalism to include transport in mixtures, and to a treatment of higher order, and nonlinear transport processes.
- e) To study the structure of the fractal repeller for interesting cases where, as a consequence of long time tail effects, transport processes are anomalous, such as two dimensional fluid systems [32].
- f) To establish the connection between the escape-rate formalism for transport and the Gaussian thermostat formalism of Hoover and Posch [3], and of Evans, Morris, Cohen, and coworkers [4, 5]. The Gaussian thermostatted systems belong to a class of dynamical systems which are time reversible without being volume preserving. The characteristic quantities describing chaos in these thermostatted systems have been described in [6, 33].

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Appendix A: The Case of Chemical Reactions

A.1. Summary of thermodynamic results

For a chemical reaction like



the numbers of particles of the reactants and products are changing at each step of the reaction according to

$$\frac{\Delta N_1}{\nu_1} = \frac{\Delta N_2}{\nu_2} = \dots = \frac{\Delta N_c}{\nu_c} = \Delta N^{(r)} , \quad (\text{A.2})$$

where $\nu_{\gamma} = \nu_{\gamma}^{-} - \nu_{\gamma}^{+}$ are the stoichiometric coefficients [34]. The degree of progress of the reaction can be measured in terms of the variation of the number $N^{(r)}$ characterizing the reaction. We also introduce the chemical concentrations, $C_{\gamma} = N_{\gamma}/V$. At the phenomenological level of thermodynamics, the velocity of the reaction is defined by

$$\dot{C}^{(r)} = \frac{\dot{\bar{C}}_{\gamma}}{\nu_{\gamma}} = w , \quad (\text{A.3})$$

where \bar{C}_{γ} are the average chemical concentrations [34]. The dependence of the reaction velocity on the concentrations themselves is given by the mass action law [34, 35]

$$w = k_{+} \prod_{\gamma=1}^c C_{\gamma}^{\nu_{\gamma}^{+}} - k_{-} \prod_{\gamma=1}^c C_{\gamma}^{\nu_{\gamma}^{-}} . \quad (\text{A.4})$$

The affinity of the reaction is defined by

$$A = - \sum_{\gamma=1}^c \nu_{\gamma} \mu_{\gamma} = - k_B T \ln \prod_{\gamma=1}^c \left(\frac{C_{\gamma}}{C_{\gamma}^{\text{eq}}} \right)^{\nu_{\gamma}} , \quad (\text{A.5})$$

where $\mu_\gamma = \mu_\gamma^0 + k_B T \ln C_\gamma$ is the chemical potential of the species γ and it is known that the affinity vanishes at thermodynamic equilibrium: $A^{\text{eq}} = 0$ [34, 35]. Near the thermodynamic equilibrium, both the reaction velocity w and the affinity A can be expanded in terms of the variations of the chemical concentrations around their equilibrium values, $C_\gamma = C_\gamma^{\text{eq}} + \Delta C_\gamma$. In the linear approximation, we obtain the equality

$$w \simeq w_+^{\text{eq}} \frac{A}{k_B T}, \quad \text{with} \quad w_+^{\text{eq}} = k_+ \prod_{\gamma=1}^c C_\gamma^{\text{eq}}, \quad (\text{A.6})$$

which allows us to obtain the Onsager coefficient of this chemical process

$$w \simeq \frac{LA}{T}, \quad \text{with} \quad L = \frac{w_+^{\text{eq}}}{k_B}. \quad (\text{A.7})$$

Yamamoto [36] and, later, Zwanzig [37] have shown that the Onsager coefficient of the chemical reaction is given by the following integral of the autocorrelation function in a classical system

$$L = \frac{1}{Vk_B} \int_0^\infty \langle \dot{N}_0^{(\text{r})} \dot{N}_t^{(\text{r})} \rangle dt, \quad (\text{A.8})$$

where the corresponding flux is here proportional to the time derivative of the number $N^{(\text{r})}$ of particles which is characteristic of the reaction. Accordingly, we obtain the result given in Table I for the reaction coefficient

$$\alpha = \frac{w}{A} = \frac{L}{T}, \quad (\text{A.9})$$

with $\langle N^{(\text{r})} \rangle = N^{(\text{r}),\text{eq}}$.

A.2. Master equation approach

The escape-rate formula can be obtained for chemical reactions by using the master equation approach [35]. As an example, we consider the isomerization



The numbers of particles A and B are the random variables of this process. The total number of particles is conserved, $N_A + N_B = N = N_{\text{tot}}$, so that the process is completely determined by the knowledge of the number of particles A . The evolution equation of the probability $P(N_A)$ that the system contains N_A particles is [35]

$$\begin{aligned} \frac{d}{dt} P(N_A) = & k_+(N_A + 1) P(N_A + 1) + k_-(N - N_A + 1) P(N_A - 1) \\ & - k_+ N_A P(N_A) - k_- (N - N_A) P(N_A) . \end{aligned} \quad (\text{A.11})$$

Introducing the fraction $0 \leq f = N_A/N \leq 1$ of particles A and defining a probability density which is function of this continuous concentration according to $p(f) = p(N_A/N) = P(N_A)$, we use Taylor expansions in the master equation (A.11) to obtain the Fokker-Planck equation

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial f} (\dot{f} p) = \frac{\partial}{\partial f} \left[D(f) \frac{\partial p}{\partial f} \right] , \quad (\text{A.12})$$

where

$$\dot{f} = -k_+ f + k_-(1 - f) + \mathcal{O}(1/N) , \quad (\text{A.13})$$

is the macroscopic rate equation while

$$D(f) = \frac{1}{2N} \left[k_+ f + k_- (1 - f) \right], \quad (\text{A.14})$$

is a concentration-dependent diffusion coefficient. This Fokker-Planck equation determines the time evolution of the probability density of a stochastic process in which the amplitude of the noise is proportional to $1/\sqrt{N}$. Let us consider these thermodynamic fluctuations around the equilibrium concentration

$$f^{\text{eq}} = \frac{k_-}{k_+ + k_-}, \quad (\text{A.15})$$

in the vicinity of which the Fokker-Planck equation becomes a diffusion equation

$$\frac{\partial p}{\partial t} = D(f^{\text{eq}}) \frac{\partial^2 p}{\partial f^2}, \quad (\text{A.16})$$

with

$$D(f^{\text{eq}}) = \frac{k_+ k_-}{N(k_+ + k_-)}. \quad (\text{A.17})$$

On this ground, we can apply the argument of first passage for the Helfand moment associated with the chemical reaction, which is given in Table I

$$G^{(\text{r})} = \frac{1}{\sqrt{V k_{\text{B}} T}} (N_A - N_A^{\text{eq}}). \quad (\text{A.18})$$

The diffusion coefficient (A.17) shows that the moment $G^{(\text{r})}$ is a random variable of Brownian type in a small neighborhood of the thermodynamic equilibrium. Indeed, the moment is related to the fraction $f = N_A/N$ of particles A according to

$$G^{(r)} = \frac{N}{\sqrt{V k_B T}} (f - f^{\text{eq}}) . \quad (\text{A.19})$$

We are looking for the first time at which the moment reaches the boundaries of the interval

$$-\frac{\chi}{2} < G^{(r)} < +\frac{\chi}{2} . \quad (\text{A.20})$$

This first-passage problem corresponds to the first escape of the fraction f out of the interval

$$f^{\text{eq}} - \frac{\varepsilon}{2} < f < f^{\text{eq}} + \frac{\varepsilon}{2} , \quad (\text{A.21})$$

with

$$\varepsilon = \frac{\sqrt{V k_B T}}{N} \chi . \quad (\text{A.22})$$

We consider a statistical ensemble formed by copies of the system and we count the number of copies which remain within the interval (A.20) at time t . Since the moment $G^{(r)}$ or the fraction f follows a diffusion process, the number of copies is decaying exponentially

$$\mathcal{N}^{(r)}(t) \sim \exp[-\gamma_1^{(r)} t] , \quad (\text{A.23})$$

at a rate $\gamma_1^{(r)}$ given by

$$\gamma_1^{(r)} \simeq D(f^{\text{eq}}) \left(\frac{\pi}{\varepsilon} \right)^2 , \quad (\text{A.24})$$

in terms of the diffusion coefficient (A.17) of the thermodynamic fluctuations around equilibrium. We mention that this exponential decay is the slowest decay dominating the time evolution at long times after the faster decay modes have died out. We can replace the size

ε (A.22) of the escape interval of the variable f by the size χ of the escape interval of the corresponding Helfand moment $G^{(r)}$ and we get

$$\gamma_1^{(r)} \simeq \alpha \left(\frac{\pi}{\chi} \right)^2, \quad (\text{A.25})$$

with the rate coefficient

$$\alpha = \frac{Nk_+k_-}{Vk_{\text{B}}T(k_+ + k_-)} = \frac{w}{A}, \quad (\text{A.26})$$

so that we recover the rate coefficient (A.7) and (A.9) of the macroscopic theory since

$$w = \frac{w_+^{\text{eq}}}{k_{\text{B}}T}, \quad \text{with} \quad w_+^{\text{eq}} = k_+ C_A^{\text{eq}} = \frac{Nk_+k_-}{V(k_+ + k_-)}. \quad (\text{A.27})$$

In this way, we see the consistency of the first-passage problem applied to the thermodynamic fluctuations described by the master equation with the macroscopic theory as well as with the Green-Kubo formula. The relation to the fractal repeller of the deterministic dynamics is discussed in full generality in the main part.

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